CHEMISTRY LETTERS, pp. 819-822, 1972. Published by the Chemical Society of Japan

THE ELECTRONIC STRUCTURE OF THE CONJUGATE BASE OF 2-NAPHTHOIC ACID

Toshihiko KOSHI, Junko YOSHINO, Hitoshi TOMA, and Kazuo OTA*
Department of Chemistry, College of Science and Engineering,
Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo
*Faculty of Engineering, Tokyo College of Photography, Iiyama,
Atsugi-shi, Kanagawa

The polarized absorption spectrum of the conjugate base of 2-naphthoic acid was measured in a stretched PVA sheet. By comparing the polarized absorption spectrum with the results of the PPP calculations including a VESCF and variable β methods, we discussed the electronic structure of the conjugate base.

It is well known that a carboxylic acid releases a proton in alkaline solution and gives a conjugate base of the acid. However, there are few papers on the electronic structure of the conjugate base. In this investigation, a polarized absorption spectrum of the conjugate base of 2-naphthoic acid was obtained in a stretched PVA (polyvinyl alcohol) sheet, and the relative polrization directions of the first two electronic transitions were determined experimentally. By comparing the above-mentioned experimental results with those of semiempirical MO calculations, we discussed the electronic structure of the conjugate base.

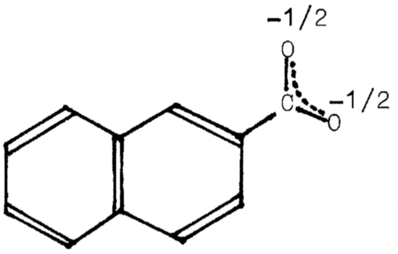
Commercially available 2-naphthoic acid (Wako Pure Chemicals Co., Ltd.) was purified by repeated recrystallizations from a mixed solvent of ethanol and water. The polarized absorption spectrum using a stretched PVA sheet was measured by the method already described.$^{1)}$

In applying the usual PPP method$^{2)}$, we have no available empirical parameters ($I_p(O^-)$, $E_a(O^-)$ and β_{CO^-}) concerning the O^- ion; so we have adopted here a VESCF$^{3)}$ and variable $\beta^{4)}$ approximations. The one-center electron repulsion integrals are evaluated by using Paoloni's equation$^{5)}$, $(rr|rr) = 3.294Z_r$, where Z_r is an effective nuclear charge determined by $Z_r = N_r - S_r - 0.35(\sigma_r + p_{rr})$, and where

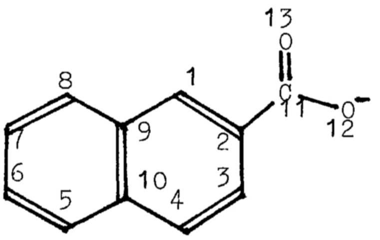
N_r is the atomic number of the r atom, S_r is a constant determined from the Slater rule, e. g. $S_r = 1.35$ for C, and $S_r = 1.0$ for O^-, σ_r is the number of valence electrons except the number of π-electrons, and p_{rr} is the π-electron density of the r atom. The two-center electron repulsion integrals, (rr|ss)'s, are evaluated by using the Nishimoto-Mataga equation.$^{6)}$ The valence state ionization potential for carbon is obtained by a parabolic relation$^{7)}$ with respect to the effective nuclear charge, $I_C(Z_C) = 3.685(Z_C)^2 - 10.008Z_C + 4.823$ eV. The ionization potentials of the O^- and $O^{-1/2}$ ions are respectively approximated by $I_{O^-\to O^+} = I_{O^-\to O} + (O^-O^-|O^-O^-)$ and $I_{O^{-1/2}\to O} = (I_{O^-\to O^+} + I_{O^-\to O})/2$, where $I_{O^-\to O} = -0.511(Z_{C^-})^2 + 17.857(Z_{O^-}) - 55.925$ eV. The resonance integrals, β_{CC} and β_{CO}, are calculated by the equations$^{4)}$, $\beta_{CC} = -0.51p_{CC} - 1.84$ and $\beta_{CO} = -0.56p_{CO} - 2.20$. The core charges for O^- and $O^{-1/2}$ are respectively taken to be +1.65 and +1.325.$^{7)}$

Figure 1 shows the polarized absorption spectrum of the conjugate base of 2-naphthoic acid. In this figure, the notations used are as follows. $D_\parallel$ and $D_\perp$; absorbances measured with the incident light polarized respectively parallel and perpendicular to the stretched direction of the PVA sheet. Rd; $D_\parallel/D_\perp$. Rs; degree of stretching the sheet. θ; orientation angle, which indicates the relative polarization direction with respect to the orientation axis of a molecule.

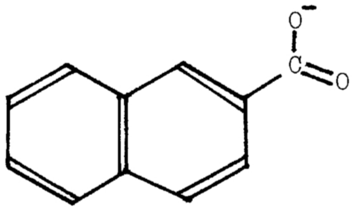
The spectrum of the conjugate base consists of three apparent bands at 30.3 kK, 34 kK and 42.8 kK. From the features of the Rd and absorption curves, the peak at 30.3 kK and the shoulder at 34 kK are considered to be the 0-0 bands of the first and the second electronic transitions, respectively. The orientation angles for both the two 0-0 bands are 55°, and this may indicate that the two bands are polarized parallel to each other. In Fig. 2 these experimental results are compared with those of the present semiempirical MO calculations. In the MO calculations, three models, I, II and III, are employed, in model I the negative charge of the conjugate base is delocalized over the two oxygen atoms, while in models II and III the negative charge is localized on the one oxygen atom.



Model I



Model II



Model III

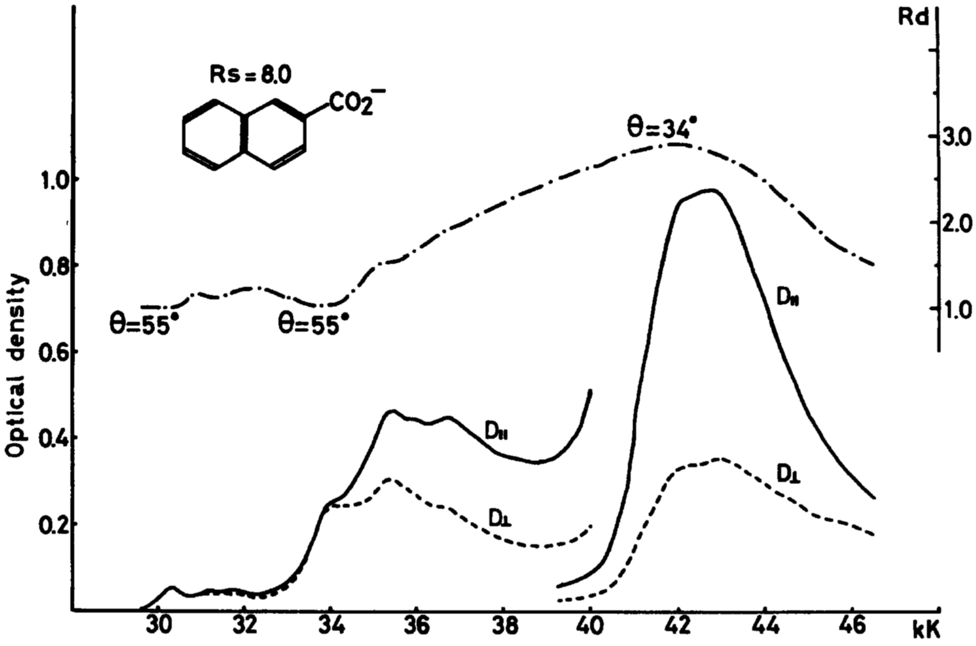


Fig. 1. The polarized absorption spectrum of the conjugate base of 2-naphthoic acid.

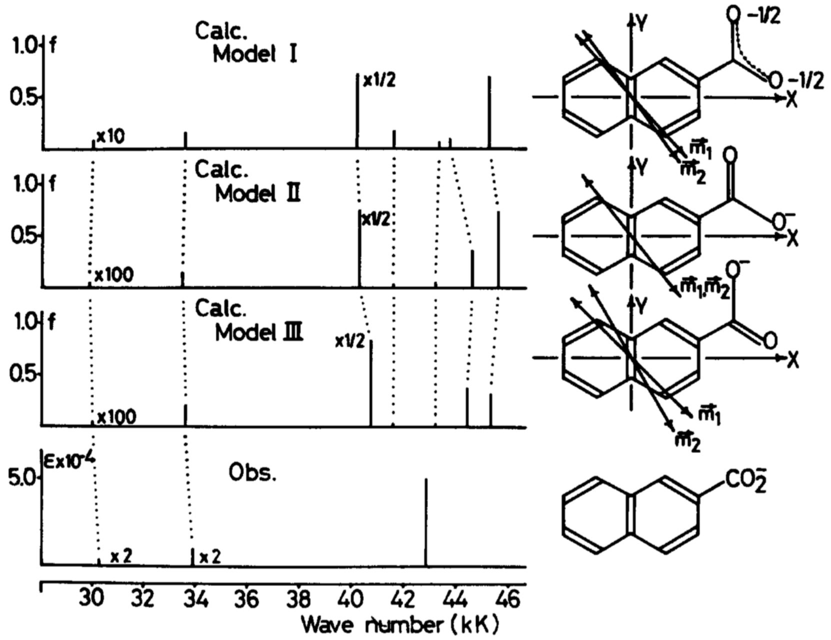


Fig. 2. A comparison of the experimental and calculated results. $\vec{m}_1$ and $\vec{m}_2$ represent the calculated polarization directions for the first and the second electronic transitions, respectively.

As for the transition energies and relative intensities, each calculated result is in satisfactory agreement with the experimental data; the differences between the theoretical and experimental transition energies for the first and the second do not exceed 0.4 kK, and there are five electronic transitions between 40 and 46 kK in each calculated result, which may be supported by the facts that the Rd values decrease in both side of the 42.8 kK band (Fig. 1). As for the polarization directions, however, the calculated results given by model II are better than those given by models I and III. The SCF values of the ionization potential and the electron affinity for the O^- ion were respectively 25.8 and 10.63 eV (model II).

From the above discussions, it may be concluded the the greater part of the negative charge of the conjugate base is localized on the one oxygen atom (at the 12 position).

REFERENCES

1) T. Hoshi and Y. Tanizaki, Z. Phys. Chem. NF, 71, 230(1970); T. Hoshi, H. Inoue, J. Shiraishi and Y. Tanizaki, Bull. Chem. Soc. Japan, 44, 1743 (1971); H. Inoue, T. Hoshi, T. Masamoto, J. Shiraishi and Y. Tanizaki, Ber. Bunsenges. Phys. Chem., 75,441(1971); H. Inoue, T. Hoshi, J. Yoshino and Y. Tanizaki, Bull. Chem. Soc. Japan, 45, 1018(1972).
2) R. Pariser and R.G. Parr, J. Chem. Phys., 21, 466, 767(1953); J. A. Pople, Proc. Phys. Soc. (London), A68, 81(1955).
3) R. D. Brown and M. L. Heffernan, Trans. Faraday Soc., 54, 757(1958).
4) K. Nishimoto and L. S. Forster, Theoret. Chim. Acta, 3, 407(1965).
5) L. Paoloni, Nuovo Cimento, 4, 410(1956).
6) K. Nishimoto and N. Mataga, Z. Phys. Chem. NF, 12, 335(1957).
7) T. Hoshi, J. Yoshino and K. Hayashi, to be published.

(Received July 6, 1972)